

PATENT ABSTRACTS OF JAPAN

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(54) POSITIVE RESIST COMPOSITION AND METHOD FOR FORMING PATTERN BY
USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a chemically amplifying positive resist composition excellent in decrease in line edge roughness, resolution and a cross-sectional profile of the resist pattern.

SOLUTION: The positive resist composition comprises: (A) a compound which generates an acid by irradiation with radiation; and (B) a resin comprising a copolymer containing (b-1) 40 to 80 mol% of a unit having an alkali soluble group, (b-2) 1 to 50 mol% of a unit having at least one acid dissociable or acid non-dissociable and alkali insoluble group, (b-3) 0 to 40 mol% of an alkali insoluble unit and (b-4) 0 to 40 mol% of a unit having an acid dissociable group but different from the unit (b-2).

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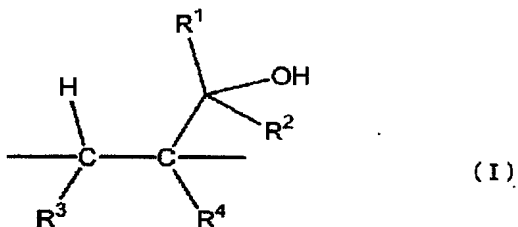
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] (A) The unit 1 which has at least one acid dissociation nature machine or the **** dissociative alkali insolubility radical expressed with the general formula (I) of the compound which generates an acid by the exposure of a radiation and the unit 40 which has (B) (b-1) alkali fusibility radical - a 80-mol % and a degree (b-2) - 50-mol %,

[Formula 1]



(Among a formula, R1 and R2 are a hydrogen atom, a **** dissociative low-grade alkyl group, or an aryl group independently, respectively, and they are an alkyl group or an aryl group a hydrogen atom and **** dissociative in R3, R4 is a hydrogen atom or -COO-R5, and R5 is the **** dissociative shape of acid dissociation nature or a chain, the letter of branching, an annular alkyl group, or a **** dissociative aryl group.)

However, neither R3 nor R4 are a hydrogen atom (b-3). Positive-resist constituent which comes to contain the resin which consists of a copolymer including a unit 0 which is a unit which has the 0-40 mol % and (b-4) acid dissociation nature machine of alkali insolubility units, and is different from (b-2) - a 40-mol unit. (However, when a unit (b-3) is more than 1 mol %, and it does not have (ii) acid dissociation nature machine, when a unit (b-2) has (i) acid dissociation nature machine, and it has an alkali insolubility radical by **** dissociative, the above-mentioned (b-4) unit is more than 1 mol %.)

[Claim 2] (b-1) The positive-resist constituent according to claim 1 whose unit is a hydroxystyrene unit or alpha-methyl hydroxystyrene unit.

[Claim 3] (b-3) The positive-resist constituent according to claim 1 or 2 whose unit is a styrene unit.

[Claim 4] The positive-resist constituent according to claim 1 to 3 whose B component is a copolymer including a unit (b-2) and a unit (b-4), whose R3 in a unit (b-2) is an aryl group and whose R4 is a hydrogen atom.

[Claim 5] (b-2) The positive-resist constituent according to claim 4 both R1 and R2 in a unit are a hydrogen atom. [whose]

[Claim 6] It is the positive-resist constituent according to claim 1 to 3 whose R3 in a unit (b-2) B component is a copolymer including a unit (b-2) and a unit (b-4), and is a hydrogen atom, whose R4 is -COO-R5 and whose R5 is straight chain-like an alkyl group or an aryl group.

[Claim 7] (b-2) The positive-resist constituent according to claim 6 whose R5 in a unit is a straight chain-like alkyl group, whose R1 is an aryl group and whose R2 is a hydrogen atom.

[Claim 8] (b-2) The positive-resist constituent according to claim 6 whose R5 in a unit is an aryl group and both R1 and whose R2 are hydrogen atoms.

[Claim 9] (b-2) The claim 1 which is the copolymer whose R4 is -COO-R5, and whose R5 R3 in a unit is a hydrogen atom, and is the letter of branching or the annular alkyl group of acid dissociation nature thru/or a positive-resist constituent given in either of 3.

[Claim 10] The positive-resist constituent according to claim 9 both R1 and whose R2 are hydrogen atoms.

[Claim 11] The positive-resist constituent according to claim 9 or 10 whose R5 is the 3rd class alkyl group.

[Claim 12] The positive-resist constituent according to claim 9 to 11 which is the copolymer which includes a unit furthermore (b-4).

[Claim 13] (b-4) Claim 1 which is at least one as which a unit is chosen from the unit which permuted the hydrogen atom of the carboxyl group of the unit which permuted the hydrogen atom of the hydroxyl group of hydroxystyrene or alpha-methyl hydroxystyrene with the acid dissociation nature machine, an acrylic acid, or a methacrylic acid with the acid dissociation nature machine thru/or either of 8, or a positive-resist constituent according to claim 12.

[Claim 14] The positive-resist constituent according to claim 13 whose acid dissociation nature machine is the 3rd class alkyl group.

[Claim 15] The positive-resist constituent according to claim 1 to 14 which furthermore comes to blend the (C) 3rd class aliphatic series low-grade amine in the 0.01 – 1.0 mass section to the (B) component 100 mass section.

[Claim 16] The positive-resist constituent according to claim 1 to 15 which furthermore comes to blend (D) organic carboxylic acid, the oxo acid of Lynn, or its derivative in the 0.01 – 1.0 mass section to the (B) component 100 mass section.

[Claim 17] (A) The positive-resist constituent according to claim 1 to 16 which is onium salt to which a component makes fluoro alkyl sulfonic-acid ion an anion [claim

18] The resist pattern formation approach which forms a resist pattern by preparing on a substrate the resist layer which consists of a positive-resist constituent indicated by claim 1 thru/or either of 17, exposing and carrying out exposure afterbaking through a mask pattern, and subsequently carrying out alkali development.

[Claim 19] The resist pattern formation approach according to claim 18 that exposure light is a KrF excimer laser.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the pattern formation approach which used a positive-resist constituent and it.

[0002]

[Description of the Prior Art] It has come to be applied also to the process as which the positive resist of the conventional non-chemistry magnification mold for i lines (365nm) was adopted as the lithography process using chemistry magnification mold POJIREJISUTO is put in practical use in recent years. Generally as for the design rule needed in such semiconductor device manufacture, the resolution near 200–300nm is demanded. In the resist pattern with which this high resolution is called for, an improvement of the Rhine edge roughness (it is called LER the uneven irregularity of a line side wall and the following.) is desired. On the other hand, in JP,5-113667,A, the chemistry magnification mold resist which used p-vinyl phenol and the copolymer of tert-butyl methacrylate as a resinous principle is proposed. Moreover, the resist constituent which has alpha-hydroxymethyl acrylate unit is indicated by JP,2000-131847,A.

[0003]

[Problem(s) to be Solved by the Invention] however, a chemistry magnification mold resist given in JP,5-113667,A — the above-mentioned duality — since the copolymer is used, there is a problem of being inferior to resolution and a profile configuration, and reduction of LER is also inadequate. Moreover, since it is inferior to definition since the alkali insolubility unit is not included, and only one has an acid dissociation nature dissolution control radical in 1 molecule further, a resist constituent given in JP,2000-131847,A runs short of the contrast of the exposure section and an unexposed part, and has the problem of being inferior to definition or a resist pattern configuration, and its reduction of LER is also inadequate. Therefore, this invention can reduce LER and offers a technical problem the positive-resist constituent of the chemistry magnification mold which is excellent in definition and a resist pattern cross-section configuration.

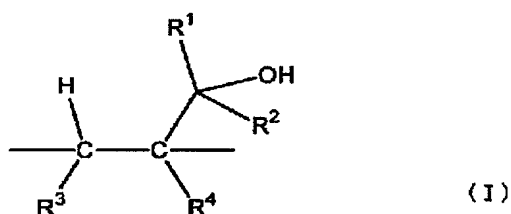
[0004]

[Means for Solving the Problem] this invention person etc. reached [that this technical problem is solvable by adopting the copolymer which has a specific unit as base resin, and] a header and this invention wholeheartedly about the above-mentioned technical problem as a result of examination. Namely, the positive-resist constituent of this invention (A) Compound [which generates an acid by the exposure of a radiation] and unit [which has (B) (b-1) alkali fusibility radical] 40 – 80-mol %, Unit 1 – 50-mol % which has at least one acid dissociation nature machine or the **** dissociative alkali insolubility radical expressed with the following general formula (I), (b-2) And (b-3) it is the unit which has the 0–40 mol % and (b-4)

acid dissociation nature machine of alkali insolubility units, and is characterized by coming to contain the resin which consists of a copolymer including a different unit 0 from (b-2) – a 40-mol unit. However, when a unit (b-2) has (i) acid dissociation nature machine, a unit (b-3) is more than 1 mol %, and when it does not have (ii) acid dissociation nature machine and has a **** dissociative alkali insolubility radical, the above-mentioned (b-4) unit is more than 1 mol %.

[0005]

[Formula 2]



[0006] (R1 and R2 are a hydrogen atom, a **** dissociative low-grade alkyl group, or an aryl group independently among a formula, respectively, an alkyl group a hydrogen atom and **** dissociative in R3 or an aryl group, and R4 are a hydrogen atom and –COO–R5, and R5 is the **** dissociative shape of acid dissociation nature or a chain, the letter of branching, an annular alkyl group, or a **** dissociative aryl group.)

However, neither R3 nor R4 are a hydrogen atom. It is here, and it combines with the radical which gives alkali fusibility, and an acid dissociation nature machine makes this radical alkali insolubility, and says the radical which can be dissociated by existence of an acid. Moreover, a **** dissociative radical means the radical which is not dissociated even if an acid exists.

[0007] Moreover, the resist pattern formation approach of this invention is characterized by forming a resist pattern by preparing a positive-resist constituent on a substrate, exposing and carrying out exposure afterbaking through a mask pattern, and subsequently carrying out alkali development.

[0008]

[Embodiment of the Invention] In the positive-resist constituent of this invention, the (A) components are the compound which generates an acid by the exposure of a radiation, and the so-called acid generator. Since the thing of varieties, such as onium salt, such as iodonium salt and sulfonium salt, oxime sulfonate, bis-alkyl or bis-aryl sulfonyl diazomethanes, nitrobenzyl sulfonate, imino sulfonate, and disulfon, is known until now, an acid generator can be used without limiting especially from such a well-known acid generator.

[0009] In especially the positive-resist constituent of this invention, in order to make the acid dissociation nature machine in the (B) component fully dissociate, it is desirable to use the onium salt which makes an anion fluoro alkyl sulfonic-acid ion with the strong reinforcement of the acid generated more. As a cation of such onium salt, the diphenyliodonium which is not permuted [a permutation or], monophenyl dialkyl sulfonium, diphenyl monoalkyl sulfonium, triphenylsulfonium, etc. are mentioned. Here, that by which the hydrogen of a phenyl group was permuted as a substitution product by one, or two low-grade alkyl groups or lower alkoxy groups or more can be shown. As said low-grade alkyl group, a methyl group, an ethyl group, propyl, n-butyl, tert-butyl, etc. can be illustrated, and a methoxy group and an ethoxy radical can be illustrated as said lower alkoxy group. It is the fluoro alkyl sulfonic-acid ion with which a part or all of a hydrogen atom of an alkyl group was fluorinated as an anion. Since the reinforcement as a sulfonic acid falls, so that a carbon number becomes long, and so that the rate of fluorination (the fluorine atom in an alkyl group comparatively) becomes small, the fluoro alkyl sulfonic acid with which all of the hydrogen atoms of the alkyl group of carbon numbers 1-10 were fluorinated is desirable.

[0010] As an example of the onium salt which makes fluoro alkyl sulfonic-acid ion an anion - Trifluoromethane sulfonate or nonafluorobutane sulfonate of diphenyliodonium, - Trifluoromethane sulfonate or nonafluorobutane sulfonate of bis(4-tert-buthylphenyl) iodonium, - Trifluoromethane sulfonate or nonafluorobutane sulfonate of triphenylsulfonium, - Trifluoromethane sulfonate or nonafluorobutane sulfonate of Tori (4-methylphenyl) sulfonium, - Trifluoromethane sulfonate or nonafluorobutane sulfonate of Tori (4-methoxyphenyl) sulfonium, - The trifluoromethane sulfonate of dimethylphenyl sulfonium, the trifluoromethane sulfonate of nonafluorobutane sulfonate methylcyclohexyl 2-oxocyclohexyl sulfonium, or nonafluorobutane sulfonate is mentioned. These may use one sort and may use two or more sorts for coincidence. (A) the loadings of a component -- the (B) component 100 mass section -- receiving -- 0.5 - 20 mass section -- it is preferably chosen in the range of 5 - 15 mass section. If pattern formation is not fully performed under in the 0.5 mass section and these loadings exceed 20 mass sections, a uniform solution will be hard to be obtained, and it becomes the cause that preservation stability falls.

[0011] In the positive-resist constituent of this invention, the (B) component is resin with which an acid dissociation nature machine dissociates according to an operation of the acid generated from the (A) component by the exposure of a radiation, consequently the solubility over alkali increases.

[0012] (b-1) As a unit, it has an alkali fusibility radical, and especially if it is the unit

which shows alkali fusibility, it will not be limited. An alkali fusibility radical is a functional group which gives alkali fusibility, such as a hydroxyl group and a carboxyl group, preferably. And (b-1) it is the unit from which the ethylene double bond of the monomer which has these functional groups and ethylene double bonds as a unit cleaves, and is obtained. Still more preferably, since it excels in dry etching-proof nature, the unit of the alkali fusibility by which this double bond cleaves and is obtained from the ethylene nature double bond which has the benzene ring is desirable. For example, a hydroxystyrene unit or alpha-methyl hydroxystyrene unit is suitable.

[0013] (b-3) A unit is a unit which shows alkali insolubility. In the positive-resist constituent of this invention, an alkali insolubility unit means a unit as the homopolymer which consists only of this unit does not indicate alkali fusibility to be. (b-3) Especially as a unit, although it does not limit, the unit from which the ethylene double bond which does not have hydrophilic radicals which give alkali fusibility, such as a hydroxyl group and a carboxyl group, but consists of an oleophilic hydrocarbon group cleaves, and is obtained is desirable. Moreover, like a unit (b-1), since it excels in dry etching-proof nature, a styrene unit is desirable. In addition, this styrene unit may be permuted by one or two low-grade alkyl groups or more (four or less carbon number).

[0014] (b-4) A unit is a unit which has an acid dissociation nature machine, and a unit (b-2) is a different unit. (b-4) A unit is a unit from which the ethylene double bond of the monomer which has preferably the functional group which gives alkali fusibility, such as a hydroxyl group and a carboxyl group, and an ethylene double bond cleaves, and is obtained, and is a unit which the acid dissociation nature machine combined with the functional group which gives alkali fusibility, and became alkali insolubility. And after an acid dissociation nature machine dissociates according to an operation of an acid, it is the unit which has a radical used as alkali fusibility. At least one chosen from the unit which permuted the hydrogen atom of the carboxyl group of the unit which permuted the hydrogen atom of the hydroxyl group of hydroxystyrene or alpha-methyl hydroxystyrene with the acid dissociation nature machine, an acrylic acid, or a methacrylic acid with the acid dissociation nature machine as such a unit is desirable on industry. The 3rd class alkyl group which is a letter of branching or an annular alkyl group, and has the 3rd class carbon as an acid dissociation nature machine is mentioned. It is desirable from being able to illustrate as the 3rd class alkyl group as what has tert-butyl, 1-methyl cyclopentyl group, 1-ethyl cyclopentyl group, 1-methylcyclohexyl radical, 1-ethyl cyclohexyl radical, desirable 2-methyl

adamanthyl radical, desirable 2-ethyl adamanthyl radical, etc., and tert-butyl being excellent in definition etc. also in especially inside. The unit guided as a unit (b-4) especially from the unit and tert-butyl methacrylate which permuted the hydrogen atom of the hydroxyl group of hydroxystyrene or alpha-methyl hydroxystyrene by the 3rd class alkyl group like tert-butyl, or tert-butyl acrylate is desirable.

[0015] (b-2) A unit is expressed with the above-mentioned general formula (I). In addition, although it does not necessarily understand clearly, it is conjectured to have contributed to the improvement of LER in the positive-resist constituent of this invention that the hydroxyl content side chain has combined with the carbon atom which constitutes the principal chain in a unit (b-2). (b-2) A unit has at least one acid dissociation nature machine or a **** dissociative alkali insolubility radical. And desirable conditions change with following two cases.

(i) -- the mol of all the units from which the above-mentioned (b-3) unit constitutes a copolymer when it has an acid dissociation nature machine -- a number -- receiving -- more than 1 mol % -- desirable -- more than 5 mol % -- it is less than [40 mol %] substantially.

(ii) -- the mol of all the units from which the above-mentioned (b-4) unit constitutes a copolymer when it does not have an acid dissociation nature machine and has a **** dissociative alkali insolubility radical -- a number -- receiving -- more than 1 mol % -- desirable -- more than 5 mol % -- it is less than [40 mol %] substantially.

[0016] In R1 and R2, with a carbon number of four or less alkyl groups, such as a methyl group, an ethyl group, and a propyl group, are mentioned as a low-grade alkyl group. A phenyl group, benzyl, a phenethyl radical, etc. are mentioned as this aryl group. In R3, as an alkyl group, a with a carbon number of four or less alkyl group, the low-grade alkyl group preferably illustrated by R1 and R2, and the same alkyl group are mentioned, and the same thing as the aryl group illustrated by R1 and R2 also as an aryl group can be mentioned. The alkyl group and aryl group which are coupled directly with a carbon atom like R1, R2, and R3 are **** dissociative, and alkali insolubility becomes high, so that a carbon number increases. Therefore, an aryl group can be called typical alkali insolubility radical.

[0017] When R4 is -COO-R5, it sets to R5. As an alkyl group A with a carbon number of 20 or less alkyl group, for example, a methyl group, an ethyl group, n-propyl group, An isopropyl group, n-butyl, sec-butyl, tert-butyl, n-pentyl radical, an isopentyl radical, a tert-pentyl radical, a cyclopentyl group, 1-methyl cyclopentyl group, 1-ethyl cyclopentyl group, a cyclohexyl radical, 1-methylcyclohexyl radical, 1-ethyl cyclohexyl radical, a heptyl radical, An octyl radical, an adamanthyl radical, 1-methyl

adamanthyl radical, 1-ethyl adamantyl radical, 2-methyl adamantyl radical, 2-ethyl adamantyl radical, a norbornyl radical, a methylation norbornyl radical, etc. are mentioned. As this aryl group, the same thing as R1, R2, and R3 is mentioned.

[0018] In the case of the 3rd class alkyl group in which R5 has the 3rd class carbon by the letter of branching, or the annular alkyl group, it acts as an acid dissociation nature machine, and, the case where it is not the 3rd class alkyl group which has the 3rd class carbon by the letter of branching, or the annular alkyl group, and in the case of-like [straight chain], acts as a **** dissociative radical conversely.

[0019] By the way, in the positive-resist constituent of this invention, the unit (b-1) which has an alkali fusibility radical raises the alkali solubility of an exposure part with the unit which has an acid dissociation nature machine. On the other hand, an alkali insolubility unit maintains the alkali insolubility for an unexposed part with the unit which has the acid dissociation nature machine in a part for an unexposed part which has not been dissociated. Therefore, the increase of contrast and definition improve. Therefore, as for the copolymer used by this invention, it is desirable to have ** for any of the unit which has an alkali fusibility radical, an alkali insolubility unit, and the unit which has an acid dissociation nature machine. (b-2) When a unit does not have an acid dissociation nature machine but has a **** dissociative alkali insolubility radical, it is necessary to include the unit which otherwise has an acid dissociation nature machine. Then, a unit (b-4) is needed. In this case, the unit which is an alkali insolubility unit (b-3) is not indispensable. (b-2) When a unit has an acid dissociation nature machine, it is necessary to include an alkali insolubility unit in others. Then, a unit (b-3) is needed. In this case, the unit which has an acid dissociation nature machine (b-4) is not indispensable. In addition, since the contrast of the exposure section and an unexposed part improves and it excels in definition and a pattern configuration more when a copolymer has two or more sorts of acid dissociation nature machines in this case, when (b-2) includes further the unit which has another acid dissociation nature machine (b-4), it is more desirable.

[0020] (B) In a component, as for a unit (b-1), it is desirable that it is 40-80-mol % to the number of mols of all the units that constitute a copolymer, and it is more desirable that it is [45-65 mol] %. (b-1) When a unit becomes inadequate [development nature] for it to be less than [40 mol %] and 80-mol % is exceeded, there is a possibility that film decrease may become large. (B) In a component, as for a unit (b-2), it is desirable that it is 1-50-mol % to the number of mols of all the units that constitute a copolymer, and it is more desirable that it is [5-25 mol] %. (b-2) When a unit becomes inadequate [the improvement nature of LER] for it to be less

than [1 mol %] and 50-mol % is exceeded, there is a possibility that definition may fall. (B) In a component, it is desirable that a unit (b-3) is less than [40 mol %] to the number of mols of all the units that constitute a copolymer, and it is more desirable that it is less than [30 mol %]. (b-2) the case where a unit (b-2) has an acid dissociation nature machine although you may not be when a unit does not have an acid dissociation nature machine and it has a **** dissociative alkali insolubility radical -- more than 1 mol % -- it is blended. In this case, there is a possibility of becoming what is inferior in definition in it being less than [1 mol %]. (b-3) When a unit exceeds 40-mol %, there is a possibility that development nature may fall. (B) In a component, it is desirable that a unit (b-4) is less than [40 mol %] to the number of mols of all the units that constitute a copolymer, and it is more desirable that it is less than [25 mol %]. the case where a unit (b-2) does not have an acid dissociation nature machine, and it has a **** dissociative alkali insolubility radical although you may not be when a unit (b-2) has an acid dissociation nature machine as stated previously -- more than 1 mol % -- it is blended. In this case, there is a possibility that a pattern cannot be formed as it is less than [1 mol %]. (b-4) When a unit exceeds the above-mentioned upper limit, there is a possibility that pattern formation may get worse.

[0021] Below, the more desirable example of - (b1) (b6) is shown about the (B) component.

(b1) : (b-2) -- the case where R3 in a unit is aryl groups, such as **** dissociative, for example, a phenyl group etc., and R4 is a hydrogen atom -- a unit (b-4) -- more than 1 mol % -- the included copolymer is mentioned.

: (b2) It is more desirable in it setting further (b1) and both R1 and R2 in a unit (b-2) being a hydrogen atom.

(b3) : (b-2) -- R3 in a unit -- a hydrogen atom -- it is -- R4 -COO-R5 -- it is -- the mol of the alkyl group of the shape of a straight chain **** dissociative in R5 or an aryl group, and all the units that are a low-grade alkyl group and benzyl similarly, and constitute a copolymer for a unit further (b-4) with R1, R2, and R3 having more specifically shown -- a number -- receiving -- more than 1 mol % -- the included copolymer is mentioned.

(b4) It is more desirable in it setting further (b3), R5 being the alkyl group of the shape of a **** dissociative straight chain, R1 being an aryl group, and R2 being a hydrogen atom, and still more desirable in R5 being a methyl group, R1 being a phenyl group, and R2 being a hydrogen atom.

: (b5) It is more desirable again in R5 being a **** dissociative aryl group, and both R1

and R2 being hydrogen atoms in (b3), and R5 is benzyl and it is still more desirable in both R1 and R2 being hydrogen atoms.

: (b-2) (b6) The copolymer whose R4 is $-\text{COO}-\text{R5}$ and whose R5 R3 in a unit is a hydrogen atom, and is the letter of branching or the annular alkyl group of acid dissociation nature is mentioned.

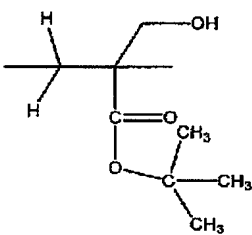
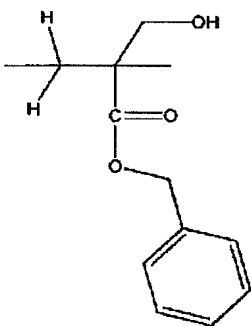
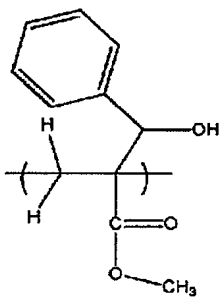
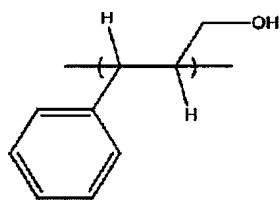
[0022] (b6) is excellent in definition and a resist pattern configuration, and the most desirable in the above (b1) of $-(b6)$. It is more desirable in furthermore both R1 and R2 being hydrogen atoms in this case. Also in (b6), it is desirable that R5 is the 3rd class alkyl group, tert-butyl, 1-methyl cyclopentyl group, 1-ethyl cyclopentyl group, 1-methylcyclohexyl radical, 1-ethyl cyclohexyl radical, 2-methyl adamantyl radical, 2-ethyl adamantyl radical, etc. are more desirable, and it is desirable especially from tert-butyl being excellent in definition etc. especially.

[0023] (B) As a component, it is resin of (b6) and the copolymer which has a unit further (b-4) is desirable from having the description of excelling in definition and a profile configuration. Two or more sorts of these (B) components may be mixed, and they may use the copolymer with which the rates of each unit differ. A mass ratio in case two sorts are mixed has the good range of 1:9 thru/or 9:1.

[0024] First, a desirable (b-2) unit is illustrated concretely below.

[0025]

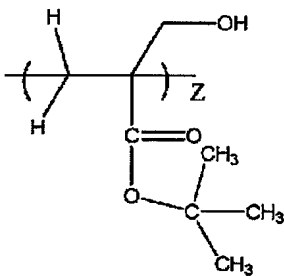
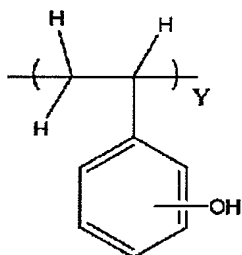
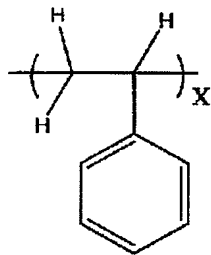
[Formula 3]



[0026] Next, the copolymer of the (B) component is illustrated concretely.

[0027]

[Formula 4]

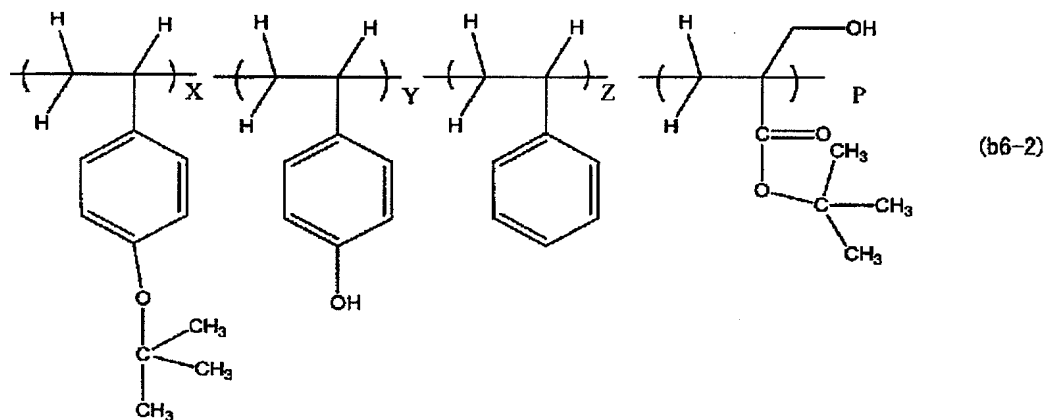


(b6-1)

[0028] in addition, a formula (b6-1) -- setting -- X -- 1-40-mol % -- desirable -- 5-35-mol % and Y -- 40-80-mol % -- desirable -- 50-65-mol % and Z -- 5-50-mol % -- it is 5-25-mol % preferably. moreover, mass average molecular weight -- 2000-50000 -- it is 3000-15000 preferably.

[0029]

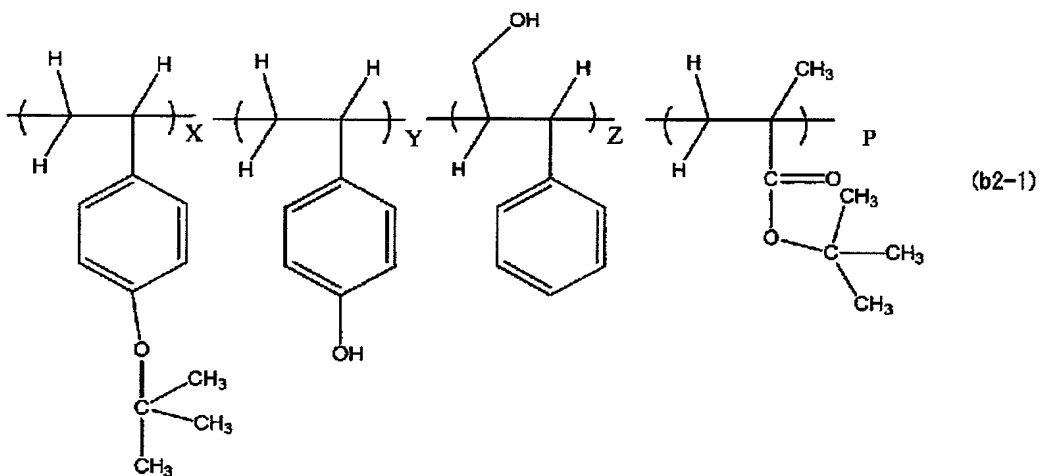
[Formula 5]



[0030] in addition, a formula (b6-2) -- setting -- X -- 0-40-mol % -- desirable -- 5-30-mol % and Y -- 40-80-mol % -- desirable -- 50-65-mol % and Z -- 1-40-mol % -- desirable -- 5-30-mol % and P -- 5-50-mol % -- it is 5-25-mol % preferably. moreover, mass average molecular weight -- 2000-50000 -- it is 3000-15000 preferably.

[0031]

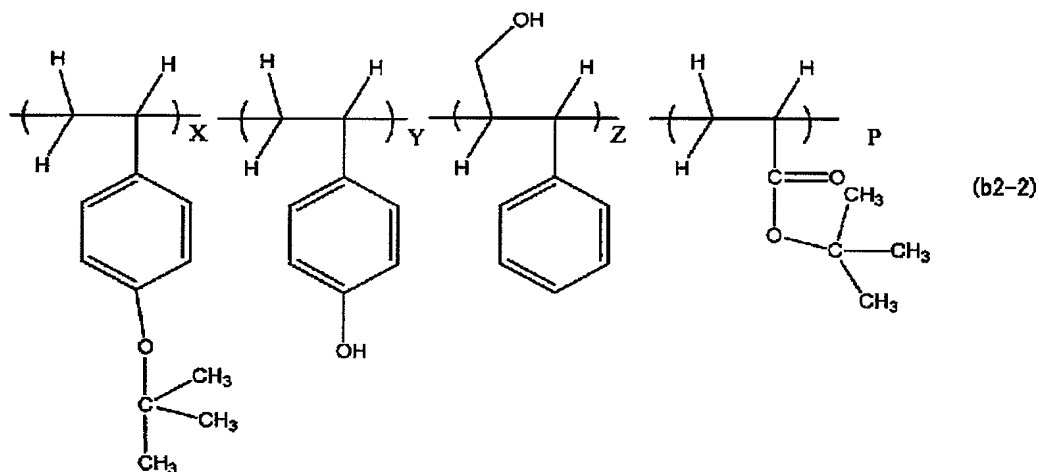
[Formula 6]



[0032] in addition, a formula (b2-1) -- setting -- X -- 0-40-mol % -- desirable -- 5-40-mol % and Y -- 40-80-mol % -- desirable -- 50-65-mol % and Z -- 1-40-mol % -- desirable -- 5-30-mol % and P -- 5-50-mol % -- it is 5-25-mol % preferably. moreover, mass average molecular weight -- 2000-50000 -- it is 3000-15000 preferably.

[0033]

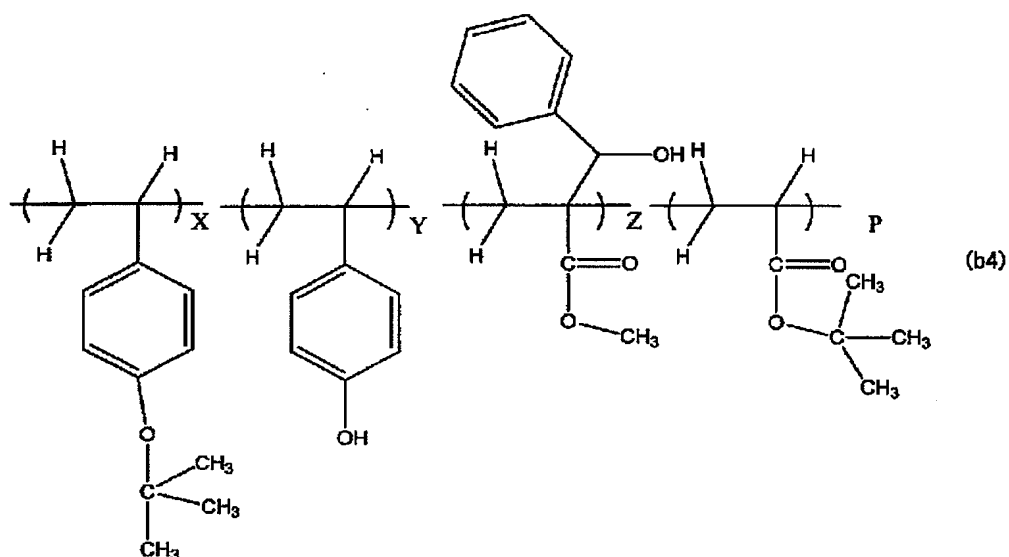
[Formula 7]



[0034] in addition, a formula (b2-2) -- setting -- X -- 0-40-mol % -- desirable -- 5-30-mol % and Y -- 40-80-mol % -- desirable -- 50-65-mol % and Z -- 1-40-mol % -- desirable -- 5-30-mol % and P -- 5-50-mol % -- it is 5-25-mol % preferably. moreover, mass average molecular weight -- 2000-50000 -- it is 3000-15000 preferably.

[0035]

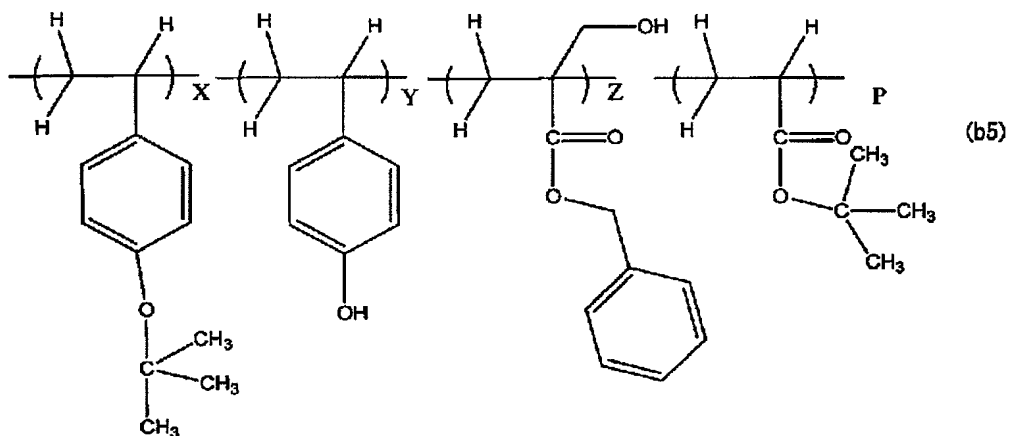
[Formula 8]



[0036] in addition, a formula (b4) -- setting -- X -- 0-40-mol % -- desirable -- 5-30-mol % and Y -- 40-80-mol % -- desirable -- 50-65-mol % and Z -- 1-40-mol % -- desirable -- 5-30-mol % and P -- 5-50-mol % -- it is 5-25-mol % preferably. moreover, mass average molecular weight -- 2000-50000 -- it is 3000-15000 preferably.

[0037]

[Formula 9]



[0038] in addition, a formula (b5) -- setting -- X -- 0-40-mol % -- desirable -- 5-30-mol % and Y -- 40-80-mol % -- desirable -- 50-65-mol % and Z -- 1-40-mol % -- desirable -- 5-30-mol % and P -- 5-50-mol % -- it is 5-25-mol % preferably. moreover, mass average molecular weight -- 2000-50000 -- it is 3000-15000

preferably. (b6-2) is the most desirable among what was concretely illustrated as these (B) components. In addition, that to which copolymerization of (b-1) and (b-2) (b-3) the well-known acrylic monomers of an except and styrene, or those derivatives was carried out in the range which does not spoil the purpose of this invention as a copolymer which constitutes the (B) component may be used.

[0039] The (C) 3rd class aliphatic series low-grade amine can be further blended with the positive-resist constituent of this invention for the purpose of diffusion prevention of too much acid etc. The amine of with a carbon number of five or less alkyl or alkyl alcohol is desirable, and as this 3rd class aliphatic series low-grade amine, low-grade fatty amine has especially a desirable thoria RUKANORU amine here, although a trimethylamine, triethylamine, tree n propylamine, Tori Ben Chill Amin, triethanolamine, tree n-propanolamine, tri-isopropanolamine, etc. are mentioned. These may be used independently and may be used combining two or more sorts. (C) When blending a component, it is desirable the 0.01 – 1.0 mass section and to blend by 0.01 – 0.5 mass % more preferably to the (B) component 100 mass section. (C) If a component is blended, the positive-resist constituent obtained will serve as high definition. The effectiveness of the combination of the (C) component by loadings being under the 0.01 mass section is inadequate, and if it adds exceeding the 1.0 mass sections, since sensibility will deteriorate, it is not desirable.

[0040] Moreover, it is the purposes, such as sensibility degradation, a substrate dependency improvement, etc. by (C) component addition, and (D) organic carboxylic acid, the oxo acid of Lynn, or its derivative can be further blended with the positive-resist constituent of this invention. A salicylic acid and a maleic acid can be illustrated as an organic carboxylic acid. Moreover, phenylphosphonic acid and a phosphoric acid can be illustrated as the oxo acid of Lynn, or its derivative. (D) When blending a component, it is desirable to blend in the 0.01 – 1.0 mass section to the (B) component 100 mass section. (D) If a component is blended, a resist pattern dependency [as opposed to a substrate in the positive-resist constituent obtained] will become small by high sensitivity. (D) component blending effect is inadequate in loadings being under the 0.01 mass section, and if it adds exceeding the 1.0 mass sections, since film decrease will serve as size, it is not desirable.

[0041] The positive-resist constituent of this invention can be made to carry out addition content of the surfactant for raising the additional resin for improving the engine performance of the additive which has a miscibility by request further, for example, the resist film, and spreading nature, a dissolution inhibitor, a plasticizer, a stabilizer, a coloring agent, the antihalation agent, etc.

[0042] The positive-resist constituent of this invention is used as a solution made to dissolve the aforementioned (A) component and the (B) component in an organic solvent. under the present circumstances, the thing which can dissolve both the above-mentioned components and can be used as a uniform solution as an organic solvent to be used -- it is -- ****ing -- the thing of the arbitration out of a thing conventionally well-known as a solvent of a chemistry magnification mold resist -- one sort -- or it can choose suitably and two or more sorts can be used.

[0043] As an example of such an organic solvent, an acetone, a methyl ethyl ketone, Ketones, such as a cyclohexanone, methyl isoamyl ketone, and 2-heptanone Ethylene glycol and ethylene glycol mono-acetate, a diethylene glycol, Diethylene-glycol mono-acetate, propylene glycol, and propylene glycol mono-acetate, The monomethyl ether of dipropylene glycol or dipropylene glycol mono-acetate, Polyhydric alcohol, such as the monoethyl ether, the monopropyl ether, the monobutyl ether, or the monophenyl ether, and the derivative of those, Ester, such as ring type ether like dioxane, methyl lactate, ethyl lactate, methyl acetate and ethyl acetate, butyl acetate, pill pinic acid methyl, pill pinic acid ethyl, methoxy methyl propionate, and ethoxy ethyl propionate, can be mentioned. These organic solvents may be used independently and may be used as two or more sorts of partially aromatic solvents. As a partially aromatic solvent, it is desirable to use the partially aromatic solvent of propylene-glycol-monomethyl-ether acetate and lactate. As for a mixed ratio, it is desirable that it is 8:2-2:8.

[0044] In the pattern formation approach of this invention, as a substrate, if it is the substrate used in this field, any substrates can usually be used. As the example, semiconductor wafers, such as a silicon wafer, GaAs, and AlGaAs, etc. can be illustrated, for example. This substrate has the desirable thing to depend on a hexamethyl silazane etc. and which is done for surface hydrophobing processing so that the adhesion of a resist layer may be raised. Especially as an approach of preparing a resist layer on this substrate, it is not limited and well-known approaches, such as the spinner coat method, a dip coating method, the flow coat method, and screen printing, can be adopted. In this way, the resist layer prepared on the substrate usually performs prebake. That is, it is desirable to give 100-140-degree C prebake for 60 - 90 seconds preferably for 40 - 120 seconds.

[0045] A radiation is exposed by only the field to which the resist layer was chosen by exposing a radiation through a mask pattern in the resist layer on this substrate. Especially as a mask pattern used here, it is not limited and conventionally idiomatic things, such as a hard surface mask blank which has the protection-from-light section

which consists of a metal thin film, can be used. Since it can obtain a good resist pattern if a KrF excimer laser, an ArF excimer laser, g line, i line, an X-ray, an electron ray, etc. can be used for the radiation used for exposure and a KrF excimer laser is used, it is desirable. Although exposure afterbaking (PEB) is performed in order to promote the reaction of the acid and acid dissociation nature machine which were generated by exposure, and it is performed at the temperature suitably set up according to the class of resist constituent etc., it gives preferably 100–150-degree C PEB (exposure afterbaking) for 60 – 90 seconds for 40 – 120 seconds, for example. Subsequently, the alkali development of this is carried out using an alkali developer, for example, a 0.1 – 10 mass % tetramethylammonium hydroxide water solution. Thus, a resist pattern faithful to a mask pattern can be obtained.

[0046]

[Example] An example is used for below and this invention is explained to it in more detail.

(Example 1)

Component : (A) Dimethyl monophenyl sulfonium nonafluorobutane sulfonate 2.5 mass section (B) component: Copolymer resin which consists of each following unit (the mass average molecular weight 5500, number average molecular weight 3400, Mw/Mn ratio 1.61) [equivalent to a formula (b5)] The 100 mass sections Hydroxystyrene unit 54-mol % alpha-hydroxy methylacrylic acid benzyl unit Ten-mol % tert-butoxy styrene unit Ten-mol % It reaches. tert-butyl acrylate unit 15-mol % (C) component : Tri-isopropanolamine 0.12 mass section (D) component : Phenylphosphonic acid A 0.10 mass section (above-mentioned A) – (D) component is dissolved in the ethyl lactate 700 mass section. After adding R08 (a trade name, the Dainippon Ink chemistry company make) which is furthermore the surfactant of a fluorine silicone system 1.0%, it filtered through the membrane filter of 0.2 micrometers of apertures, and the positive-resist solution was obtained.

[0047] Subsequently, prebake of the above-mentioned positive-resist solution was carried out to the substrate which gave the adhesion promoter coat to the 8 inch silicon wafer for 90 seconds at 120 degrees C behind the spin coat, and the resist layer of 500nm of thickness was formed. After irradiating alternatively the substrate which formed this resist layer using contraction projection aligner NSR-S203B (the NIKON CORP. make, NA=0.6), PEB processing during 90 seconds of the KrF excimer laser was carried out at 130 degrees C at it. Subsequently, paddle development of this substrate was carried out for 60 seconds at 23 degrees C with the 2.38 mass % tetramethylammonium hydroxide water solution, and the resist pattern of a positive

type was obtained. Thus, 250nm Rhine and the tooth-space pattern which were obtained, and the 250nm isolated Rhine pattern were resolved in the good configuration. The 250 morenm slit pattern was also resolved in the good configuration. Moreover, all the light exposure (sensibility) taken to form these patterns was 31 mJ/cm². Moreover, it was 6.9nm when LER of a 250nm Rhine and a tooth-space pattern was calculated.

[0048] (Example 2) Copolymer resin B-1 (the mass average molecular weight 5100, number average molecular weight 3000, Mw/Mn ratio 1.70) which consists of each following unit as a (B) component [equivalent to a formula (b6-2)] 50 mass sections, Except having used the copolymer-resin B-2 (mass average-molecular-weight 4900, number-average-molecular-weight 28000, Mw/Mn ratio 1.75) [equivalent [to a formula (b6-2)]] 50 mass section, like the example 1, the positive resist was prepared and the regist patterning same subsequently as an example 1 was performed.

(B-1) Hydroxystyrene unit 15 mol % of 48-mol % and alpha-hydroxy methylacrylic acid-tert-butyl units, Styrene unit 20-mol % and a tert-butoxy styrene unit 17 mol % (B-2) hydroxystyrene unit 51-mol %, alpha-hydroxy methylacrylic acid-tert-butyl unit Five-mol %, Styrene unit 25-mol % And tert-butoxy styrene unit 19-mol Rhine (% , thus obtained 250nm) and a tooth-space pattern, and the 250nm isolated Rhine pattern were resolved in the good configuration which is excellent in rectangle nature. Furthermore, the 250nm slit pattern was also resolved in the good configuration. Moreover, all the light exposure (sensibility) taken to form these patterns was 16 mJ/cm². Moreover, it was 7.9nm when LER of a 250nm Rhine and a tooth-space pattern was calculated.

[0049] (Example 1 of a comparison) Except having changed the (B) component into the copolymer-resin (mass average-molecular-weight 4900, number-average-molecular-weight 3100, Mw/Mn ratio 1.59) 100 mass section which consists of each following unit, like the example 1, the positive resist was prepared and the regist patterning same subsequently as an example 1 was performed. Hydroxystyrene unit 54-mol % and alpha-hydroxy methylacrylic acid-tert-butyl unit 15-mol % and tert-butoxy styrene unit Although 31-mol Rhine and a tooth-space pattern and a 250nm isolated Rhine pattern (% , thus obtained 250nm), and the 250 morenm slit pattern were resolved, its taper configuration was poor. Moreover, it was 13.5nm when LER of a 250nm isolated Rhine pattern was calculated.

[0050] (Example 2 of a comparison) Except having changed the (B) component into the copolymer-resin (mass average-molecular-weight 5000, number-average-molecular-weight 3100, Mw/Mn ratio 1.60) 100 mass section which

consists of each following unit, like the example 1, the positive resist was prepared and the resist patterning same subsequently as an example 1 was performed.

The taper configuration was poor although 29 mol Rhine and the tooth-space pattern and the 250nm isolated Rhine pattern (% , thus 250nm) of 20 mol % and tert-butoxy styrene units of 15 mol % and styrene units of 35 mol % and tert-butyl (alpha-hydroxymethyl) acrylic ester units of hydroxystyrene units, and the 250 morenm slit pattern were resolved. Moreover, it was 10.9nm when LER of a 250nm isolated Rhine pattern was calculated.

[0051] (b-3) In the resist constituent of the example 1 of a comparison which does not include a unit, and the example 2 of a comparison with few contents of a unit (b-1) than a convention As opposed to the taper configuration of Rhine and a tooth-space pattern, an isolated Rhine pattern, and a slit pattern being poor Since Rhine obtained in the examples 1 and 2 and the tooth-space pattern, and the isolated Rhine pattern are resolved in the good configuration and the slit pattern is also resolved in the good configuration, it turns out that the positive-resist constituent of this invention is excellent in definition and a resist pattern cross-section configuration. Moreover, it turns out that LER generating also has little LER of the isolated Rhine pattern with which LER of the isolated Rhine pattern obtained in the above-mentioned example of a comparison was obtained in the examples 1 and 2 to comparatively large one with 13.5nm and 10.9nm as for 6.9nm, 7.9nm, and the positive-resist constituent of this invention since it is small.

[0052]

[Effect of the Invention] As stated above, it is a chemistry magnification mold, and the positive-resist constituent of this invention has the description of excelling in definition and a resist pattern cross-section configuration, and there is also little Rhine edge roughness generating with Rhine and a tooth-space pattern.

[Translation done.]